

A Generalized Dielectric Polarization Evolution Equation

James Baker-Jarvis

National Institute of Standards and Technology
Boulder, CO

ABSTRACT

In this paper a non-equilibrium statistical-mechanical theory of dielectric relaxation is developed. This approach differs from previous work in that a generalized nonlocal evolution equation for the polarization is constructed. General equations of motion are presented for the polarization, internal energy, and entropy which include effects of memory. These equations can be expressed in terms of reduced-correlation functions, and are valid for non-equilibrium and arbitrary field strengths. Expressions for an effective local field also are developed. The Fourier transform of the evolution equation yields a general compact expression for the Fourier transform of the memory function and a specific form for the susceptibility. The kernel, Fourier transform of the memory function are developed, and relaxation-time functions for special cases. In the limit of a single relaxation time, a Debye response is obtained. In the subsequent special cases exponential and Gaussian forms for the memory functions are assumed. The final special case relates a power-law circuit transfer function to the theory of Dissado and Hill. In this case the memory kernel and relaxation times are derived from the Dissado-Hill response function.

1 INTRODUCTION

IN this paper, I present a theory of dielectric relaxation using non-equilibrium statistical mechanics. The statistical-mechanical foundations are addressed in terms of generalized correlation functions. The specific phenomenology of relaxation involves the estimation of correlation functions. The approach is based on a previously developed projection-operator formalism [1, 2]. This projection-operator approach to dielectric relaxation has several advantages [3–9]. This method yields an exact nonlocal polarization evolution equation without making the linear approximation, as is made in Kubo's dynamical-driving formalism. In addition, the equation can describe non-equilibrium behavior [10, 11]. In this paper a number of examples of correlation functions are considered.

Section 2 (see the Table 1 of symbols) begins with an overview of the general properties of dielectric relaxation in solids and liquids. I then develop the underlying statistical-mechanical theory and a novel polarization evolution equation. I use the results to study polarization response and develop approximations for the relaxation kernel and the Fourier transform of the memory function.

2 DIELECTRIC RELAXATION

2.1 RELAXATION

In this overview Section, the theory of dielectric relaxation is described. To this end I overview the microscopic origins of dielectric

response as well as previously developed models. In chiral materials it has been found that application of magnetic fields also can produce dielectric polarization. In this paper I do not consider magnetic field interactions.

When an electric field is applied to a material, the atoms, molecules, and defects all readjust in position. The readjustment of molecules in response to an electric field is called 'dielectric relaxation'. Relaxation behavior depends on lattice properties, frequency, and temperature.

The response of materials to applied fields depends strongly on lattice structure. The lattice order or disorder, the presence of permanent dipoles, temperature, and defects all contribute to dielectric response. Relaxation can be a result of dipolar rotation, lattice-phonon interactions in ionic solids and crystals, defect diffusion, higher multipole interactions, or motion of free charge. Hopping-charge, phonon assisted tunneling transport and accompanying low-frequency percolation behavior play a role in charge transfer relaxation [12]. In hopping conduction, percolation dominates at low frequencies and pair approximation at high frequencies. It is generally believed that dipoles reorient in an applied field in discrete jumps accompanied by the movement of charge or defects in the lattice. This occurs as the molecule makes transitions from one potential well to another. Since relaxation is due to transitions between internal energy-density states, a material does not respond instantaneously to an applied field. Transitions between states proceed probabilistically and a finite time is required for the occurrence of events. If the applied field is static then the system will eventually

Table 1. List of Symbols

Symbol	Description	Unit	Symbol	Description	Unit
A	constant	—	u_{in}	induced potential energy	J
\hat{A}	polarizability tensor	F/m	u_{dip}	dipole potential energy	J
C_l	lumped capacitance	F	u_{dp}	dipolar potential energy	J
G_l	lumped conductance	S	S	entropy, Equ.(38)	J/K
\vec{D}	displacement vector	C/m ²	\mathcal{U}	internal energy, Equ.(26)	J
\vec{E}	applied electric field	V/m	U	internal energy density, Equ.(28)	J
\vec{E}_{loc}	local electric field	V/m	V	volume	m ³
\vec{E}_P	effective electric field	V/m	Z	partition function, Equ.(32)	—
\hat{E}	Fourier transformed field	V/m	α	polarizability	F/m
F_n	phase space functions	—	β	Lagrangian multiplier	J ⁻¹
g	pulse response function	F/m-s	χ	susceptibility	F/m
K	kinetic energy	J	χ_0	freespace susceptibility	F/m
J	current density	A/m ²	ϵ	permittivity	F/m
$\mathcal{F}\{K_e\}$	memory response function	s ⁻¹	ϵ_0	freespace permittivity	F/m
K_e	memory kernel	s ²	ϵ_s	static permittivity	F/m
l	response-decay function	F/m-s	ϵ_∞	optical permittivity	F/m
\vec{m}_0	dipole moment	C-m	Γ	phase space	—
k	Boltzmann's constant	J/k	Γ_f	Gamma function	—
L	depolarization tensor	m/F	$\vec{\pi}_i$	momentum	kg-m/s
M_i	mass	kg	ω	radial frequency	s ⁻¹
q	charge	C	ω_p	reference radial frequency	s ⁻¹
\vec{p}	dipole moment density, Equ.(15)	C/m ²	ρ	statistical density operator, Equ.(97)	—
\vec{p}'	effective dipole moment density	C/m ²	Φ	response function	—
\vec{P}	polarization, Equ.(27)	C/m ²	σ_0	dc conductivity	F/m-s
\vec{r}_i	phase space point	m	σ	density operator, Equ.(31)	—
\vec{r}	field point	m	τ_e	relaxation time	s
T	temperature	K	τ_i	relaxation time i	s
T_{ij}	dipole tensor	m ³	$\vec{\mu}$	permanent moment	C-m
u_0	lattice potential energy	J	\mathcal{V}	potential energy	J

come to equilibrium. If the applied field is time dependent then the material will continuously relax in the applied field, but with a time lag.

There are many models for dielectric relaxation. These approaches can be categorized into theories based on harmonic oscillators, distribution of relaxation times and probabilistic models, Langevin equations, and models based on Liouville's equation. The formulation used in this paper falls in the latter category. The models can be divided roughly into those that include a temperature dependence from statistical mechanical reasoning, and models that neglect temperature dependence or introduce it in an ad-hoc manner. Langevin-based models such as Debye's theory include temperature dependence from statistical-mechanical theory. Many of the probabilistic models do not include temperature from first principles.

In the distribution of a relaxation time model, Debye relaxations are weighted by a probability-density function. This approach is often criticized since it is not always possible to interpret the distribution function [13]. However, the distribution of relaxation times approach is sufficiently general that most dielectric response phenomena can be described by the model. The question is whether the model lends itself to physical interpretation. Since the distribution of the relaxation times model is a generalization of the Debye response, the physical interpretation is not clear. This is because the permittivity for dipolar systems generally does not exhibit a single-pole Debye response, but rather a power-law dependence. The origin of this difference can be attributed to many-body interactions. The distribution of relaxation times model, in the end, is just an alternative causal mathematical representation of

Table 2. List of Mathematical Notations

Symbol	Description	Equation
M	confluent hypergeometric function, ${}_1F_1$	
\mathcal{L}	Liouville operator	
P	projection operator	
${}_2F_1$	hypergeometric function	
${}_2F_2$	hypergeometric function	
\dot{m}	dm/dt	(8)
\dot{m}	$i\mathcal{L}m$	(34)
$:$	contraction of tensors	(44)
\mathcal{F}	Fourier transform	(7)
$\langle F'F' \rangle$	correlation function	(103)
$\langle F' \rangle_t$	expectation at time t	(98)
i	$\sqrt{-1}$	
\mathcal{T}	evolution operator	(105)
T_F	integration over phase space	(29)
Θ	unit step function	
δ	delta function	

the permittivity and does not introduce new information.

Dielectric loss in polar materials primarily is due to friction caused by rotation of induced and permanent dipoles. Losses in nonpolar materials originate mainly from the interaction of induced dipoles, intrinsic photon-phonon interaction with the electromagnetic field, and extrinsic loss mechanisms caused by defects, dislocations, and grain structure. Loss in high-purity crystals is primarily intrinsic. A crystal vibrates harmonically in the absence of an applied electric field; however, inharmonic coupling to the electric field modifies this behavior. The inharmonic interaction allows photon-phonon interaction and thereby introduces loss [14]. It has been found that high-purity centrosymmetric

dielectric crystals, *i.e.* crystals with reflection symmetry, such as crystalline sapphire, strontium titanate or quartz, generally have lower loss than crystals with non-centrosymmetry [15].

Reasons for the widespread use of the Debye equation as a paradigm in dielectric relaxation theory is that it is simple, it models idealized relaxation, and it yields predictions on the temperature dependence of the relaxation time, if the temperature dependence of the viscosity and density are known. The depolarization current for many disordered solids is non-exponential and at short times satisfies a power law of the form [13, 16]

$$I(t) \propto t^{-n} \quad (1)$$

and satisfies a power law at long times of the form

$$I(t) \propto t^{-(1+m)} \quad (2)$$

where $0 < n, m < 1$. In this analysis, short times correspond to the high microwave region of the frequency spectrum and long times refer to frequencies < 10 kHz. At very small times the current must depart from (1) to satisfy theoretical constraints. There are exceptions to the behavior given in Equations (1) and (2), for example, in dipolar glasses and polycrystalline materials [17]. The susceptibility of many disordered solids typically behaves at high frequencies as

$$\chi'(\omega) \propto \chi''(\omega) \propto \omega^{n-1} \quad (3)$$

This implies that χ''/χ' is independent of frequency. At low frequencies [13]

$$\chi'(0) - \chi'(\omega) \propto \chi''(\omega) \propto \omega^m \quad (4)$$

This behavior implies that $\chi''/(\chi_0 - \chi')$ is a constant. On the other hand, the Debye model predicts a susceptibility loss tangent that increases linearly with frequency. Debye theory also predicts $\tan \delta = \epsilon''/\epsilon'$ to vary in proportion to ω at low frequencies, which is observed in some dipolar materials and low-loss ceramics at radio frequencies [18], and as $1/\omega$ at high frequencies.

Any theory of relaxation has to model the local field adequately. In a dielectric, the local and applied fields are not identical since charge screening produces an electric depolarization field. Many models of polar and nonpolar materials have been developed over the years which use different approximations to the local field. The Clausius-Mosotti equation was developed for noninteracting, nonpolar molecules using the Lorentz model of the internal field. This equation works well for nonpolar gases and liquids. Debye introduced a generalization of the Clausius-Mosotti equation for the case of polar molecules. Onsager developed an extension of Debye's theory by including the reaction field and a more comprehensive local field expression [19]. The Onsager equation is often used to calculate dipole moments in gases.

The Debye model of relaxation assumes that dipoles relax individually with no interaction with the local environment and neglects effects of inertia. This type of relaxation is an idealization and is rarely observed in nature. The simple harmonic oscillator equation for the polarization \vec{P} can illustrate single-pole relaxation

$$\underbrace{\frac{d^2 \vec{P}}{dt^2}}_{\text{inertial}} + \underbrace{\gamma \frac{d\vec{P}}{dt}}_{\text{damping}} + \underbrace{\frac{1}{\tau} \vec{P}}_{\text{restoring}} = \underbrace{\frac{c_0}{\tau} \vec{E}(t)}_{\text{driving}} \quad (5)$$

where the temperature-dependent relaxation time is $\tau = \nu \langle r^2 \rangle p / kT$, with viscosity ν , molecular dipole moment p , and mean-square molecular radius $\langle r^2 \rangle$; c_0 and γ are constants. Debye relaxation is obtained

from this equation by neglecting the first term which is related to inertia. Generally, inertial effects are important at very high frequencies. In order to satisfy the requirements of linear superposition, it is imperative that any linear polarization relation be time invariant; further, it must also be a causal relationship [20, 21]. The linear superposition requirement is not satisfied if the relaxation time in (5) is time dependent. This can be remedied if (5) is replaced by an integro-differential equation where the restoring and driving terms in (5) become convolutions. The evolution equation developed in this paper has this form.

Dissado, Hill, and Jonscher argue that the power-law behavior explains most dielectric response in disordered solids and that there is minimal need to invoke a Debye relaxation or a distribution of relaxation times argument [13]. Dissado and Hill conclude that non-exponential relaxation is related to cluster response [13]. In their model, molecules within a correlated region react to the applied field with a time delay. The crux of this approach is that in most condensed-matter systems the relaxation is due not to independently relaxing dipoles, but rather that the relaxation of a single dipole depends on the state of other dipoles in a cluster. This theory of disordered solids is based on charge hopping and dipolar transitions within regions surrounding a defect and between clusters [13]. The effect is to spread out the response over time and therefore to produce non-exponential behavior. Dissado and Hill developed a representation of a correlation function that includes cluster interaction. According to this theory, the time-domain response at short times is Gaussian. At still longer times are intra-cluster transitions with a power law of the form $t^{(-n)}$. At still longer times there are inter-cluster transitions with a Debye-type response, and finally a response of the form $t^{(-m-1)}$ [22]. Van Turnhout and Roussy have independently derived a distribution function that corresponds to the Dissado-Hill model [23–25]. In these studies the distribution function of relaxation times was found to be in the form of a beta function. Therefore the Dissado-Hill model can be described also by a distribution of relaxation times approach.

Dielectric relaxation, described by Kubo's linear response theory, is based on correlation functions and is an example of a relaxation theory based on Liouville's equation. The main difficulty with this approach, and for that matter, the theory developed in this paper, is that the correlation functions are difficult to calculate and approximations are usually made in numerical calculations. The linear expansion of the probability-density function in Kubo's theory also limits its usefulness for nonlinear problems.

Jonscher, Dissado, and Hill have developed theories of relaxation based on fractal self-similarity [12, 26]. Jonscher's approach is based on a screened-hopping model where response is modified due to many-body charge screening [27]. In the limit of weak screening the Debye model is recovered.

Non-exponential response has been obtained using percolation models [18]. Non-exponential response also has been reproduced in computer simulations using a correlation-function approach with coupled rate equations for chains of dipoles [9, 28, 29]. Defect-diffusion models have been developed where relaxation is related to diffusion of a defect in a solid lattice [30, 31]. In this theory it is assumed that a defect enhances the relaxation rate by allowing dipoles to rotate. Skinner

has related the defect diffusion model in polymers to soliton dynamics [31]. In this theory the defects travel in polymer chains as solitons. Other models have been proposed that are based on more complicated theories for the underlying transition probability [32–35]. These models use age-dependent transition rates where a new variable describing the age of a state is introduced to model defect diffusion processes. In models based on correlation functions, as in this paper, the ensemble averaging in the correlation function includes many of the effects of waiting times and microscopic transitions. However, the correlation functions are not, in general, easy to model.

2.2 CONSTITUTIVE RELATIONS AND THEORETICAL CONSTRAINTS

Constitutive relations between field quantities in Maxwell's equations must satisfy certain symmetries. The polarization and displacement fields are even under time reversal, and odd under parity transformations, whereas the induction and magnetic fields are odd under time reversal and even under parity transformations. Electric polarization can be adequately modeled by classical mechanics, whereas magnetic processes require a quantum-mechanical analysis [36].

In most materials, the effects of memory are important for dielectric relaxation. Memory originates from many-body interactions which tends to broaden the response of the system to the applied field and can yield non-exponential relaxation. Electromagnetic interactions can be linear or nonlinear functions of the electric field strength. In linear electrodynamic driving the polarization is expressed as a convolution of the applied field with a correlation or pulse-response function.

There are many theoretical constraints on the form of the dielectric susceptibility. The real and imaginary parts of the susceptibility for a specific relaxation process must be related by the Kramers-Kronig condition. However, in a Kramers-Kronig transformation the dc component of the conduction current in the imaginary part of the susceptibility does not contribute to the real part of the susceptibility [37, 38]. This is because the dc conduction current is assumed to respond instantaneously to an applied field as $\vec{J} = \sigma_0 \vec{E}$; this yields a singularity in the imaginary part of the susceptibility at $\omega = 0$. On the other hand, the ac and some parts of the dc conductivity can take time to build up and can influence both the real and imaginary parts of the susceptibility.

The permittivity is defined in terms of the microscopic polarization pulse-response function $g(t) = \langle \vec{P}(t) \cdot \vec{E}(0) \rangle$ where $\gamma(t)$ is the microscopic correlation function

$$\frac{(e(\omega) - \epsilon_\infty)(2\epsilon(\omega) + \epsilon_\infty)\epsilon_s}{\epsilon(\omega)(\epsilon_s + \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)} \approx \frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \int_0^\infty g(\tau) e^{-i\omega\tau} d\tau \quad (6)$$

where due to causality $g(\tau) = 0$ for $\tau < 0$ and the Fourier transform \mathcal{F} is defined as

$$\mathcal{F}\{g\}(\omega) = \int_0^\infty g(\tau) e^{-i\omega\tau} d\tau \quad (7)$$

and ϵ_s and ϵ_∞ are the static and optical limits of the permittivity. The dipole correlation function can be expressed in terms of the dipole moment \vec{m} as

$$I(t) = \frac{-\langle \vec{m}(0) \cdot \vec{m}(\cdot - t) \rangle}{\langle \vec{m}(0) \cdot \vec{m}(0) \rangle} \quad (8)$$

and is an approximation to $\gamma(t)$. In linear-system response, for a given response function, we can show that at high frequencies, near the optical limit, the real part of the susceptibility must behave as $1/\omega^2$ and the imaginary part must tend to 0 as $1/\omega^3$ [7]. This high-frequency behavior is not realized in most phenomenological radio-frequency and microwave permittivity models. These high-frequency constraints on the loss are important since the attenuation coefficient scales as $\omega\epsilon''$ where ϵ'' is the imaginary part of the permittivity. The integral of the attenuation coefficient is convergent if the imaginary part of the permittivity goes to zero faster than $1/\omega^2$ at high frequencies. This precludes the possibility of the Debye model extending into very high frequencies, since this model has an asymptotic behavior for ϵ'' of the form $1/\omega$. These high-frequency requirements assume only that the impulse-response function is analytic and that frequencies are sufficiently high that a Taylor's series expansion of (6) about $t = 0$ is valid. Fonda has shown in a quantum-mechanical analysis of decay, that at short times the decay function must go to 0 at a rate slower than exponential [39]. It can be shown also that at large times the decay must be slower than exponential. Fonda also showed that the Paley-Wiener condition prohibits the correlation function from being a pure exponential at large times [39]. The Paley-Wiener condition is a constraint on the Fourier transform of a function. In this case the Fourier transform is from the quantum-mechanical bounded energy spectrum to the time domain.

In linear driving, the response of the displacement \vec{D} and polarization \vec{P} fields to the applied field \vec{E} applied from $t = -\infty$ is expressed as

$$\vec{D}(\vec{r}, t) = \epsilon_0 \vec{E}(\vec{r}, t) + \underbrace{\chi_0 \int_{-\infty}^t g(t - \tau) \vec{E}(\vec{r}, \tau) d\tau}_{\vec{P}} \quad (9)$$

where $\chi_0 = \epsilon_s - \epsilon_\infty$ is the static susceptibility. For linear response, in the frequency domain, the displacement field is related to the incident field by

$$\vec{D}(\vec{r}, \omega) = \epsilon(\omega) \cdot \vec{E}(\vec{r}, \omega) \quad (10)$$

The effective permittivity is written as

$$\epsilon(\omega) = \epsilon_0 + \chi(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (11)$$

where ϵ_0 is the permittivity of free space and χ is the frequency-dependent susceptibility

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (12)$$

The imaginary part of the permittivity also can contain the effects of dc conduction modeled by $i\sigma_0/\omega$.

Some researchers combine the higher-order moments in the definition of the displacement field

$$\vec{D} \leftrightarrow \epsilon_0 \vec{E} + \vec{P} = \vec{\nabla} \cdot \vec{Q} \quad (13)$$

where \overleftrightarrow{Q} contains higher multipole effects [6]. The double-headed arrow in this constitutive relation indicates that the relationship could be local or nonlocal in time, that is, may contain memory. Others combine the quadrupole and higher moment terms with the polarization vector [5]. It is important that the constitutive relation be independent of reference position [40].

In actual dielectric measurements, in the frequency domain, a bulk permittivity is obtained that includes both induced and permanent dipoles and higher-moment polarization. In this analysis I assume the polarization contains only dipolar interactions.

In a system consisting of an ensemble of particles possessing permanent and induced electric moments, the local polarization \vec{p} results from both induced and permanent dipole moments and the movement of free charge. We consider the dipole moment of the i -th particle in a condensed-matter system. The permanent and induced dipole moment can be written as

$$\vec{m}_i = \vec{\mu}_i + \overleftrightarrow{\alpha}_i \cdot \vec{E}_{av(i)} \quad (14)$$

where $\vec{m}_i/V = \vec{p}_i$, V is volume, μ_i is the permanent dipole moment of the i -th particle, $\vec{E}_{av(i)}$ is the local field at the particle, and $\overleftrightarrow{\alpha}_i$ is the polarizability tensor.

Pyroelectric materials have a net permanent dipole in the absence of a field, however most materials do not have a net permanent moment. In nonpyroelectric materials, where individual molecules have permanent moments, on application of a field, fluctuations in the ensemble average of the individual molecular moments produces a net polarization.

In general, a multipole moment is unique only if all the lower moments vanish. In order to maintain uniqueness of the dipole energy we require the sum of the charge in the sample to be 0. The dipole-moment density \vec{p} , which yields the correct electric moment when integrated over the sample, is defined as [2]

$$\vec{p}(\vec{r}) = \sum_{j=1}^N \vec{r}_j q_j \delta(\vec{r}_j - \vec{r}) \quad (15)$$

where q_j is the charge at phase space position \vec{r}_j with momentum $\vec{\pi}_j$.

We assume that all moments can be written as (15). Modeling of induced moments requires knowledge of the positions of all charge in the molecules and volume. Modeling of permanent dipoles requires only knowledge of the coordinates of the dipole in which case the integrations in the expectations decouple.

3 EVOLUTION EQUATIONS

3.1 INTERNAL-ENERGY DENSITY

In our statistical-mechanical derivation we will need an expression for the Hamiltonian. In this Section we review the components of the potential energy of a system of identical particles in an electric field.

The total internal energy is a sum of kinetic and potential energies. In order to study and review the various contributions of the potential energy we consider a collection of both permanent and induced polarizations and follow Mandel and Mazur to perform an electrostatic analysis [19, 41].

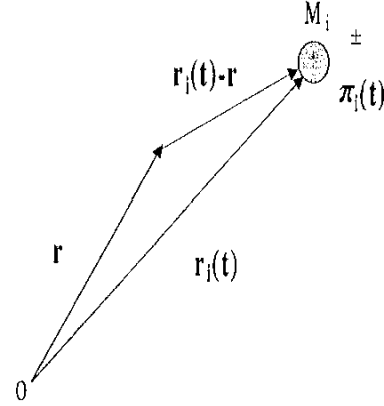


Figure 1. Dipole moment calculation.

The local electric field of particle i in the dielectric in an applied field \vec{E} , after correcting for depolarization is

$$\vec{E}_{av(i)} = \vec{E} - \sum_j \overleftrightarrow{T}_{ij} \cdot \vec{m}_j \quad (16)$$

The dipole-dipole interaction tensor is

$$\overleftrightarrow{T}_{ij} = \frac{1}{|\vec{r}'_i - \vec{r}'_j|^3} \left(\overleftrightarrow{I} - 3 \frac{(\vec{r}'_i - \vec{r}'_j)(\vec{r}'_i - \vec{r}'_j)}{|\vec{r}'_i - \vec{r}'_j|^2} \right) \quad (17)$$

where \overleftrightarrow{I} is the identity matrix. By iteration of (14) and (16) the dipole moment of the i -th particle, which includes interactions, is obtained

$$\begin{aligned} \vec{m}_i = & \underbrace{\vec{\mu}_i - \alpha \sum_j \overleftrightarrow{T}_{ij} \cdot \vec{\mu}_j + \alpha^2 \sum_{i,k \neq j} \overleftrightarrow{T}_{ij} \overleftrightarrow{T}_{jk} \cdot \vec{\mu}_k - \dots}_{\text{permanent moment}} \\ & + \underbrace{\left[\alpha \overleftrightarrow{I} \cdot \alpha^2 \sum_j \overleftrightarrow{T}_{ij} + \alpha^3 \sum_{i,k \neq j} \overleftrightarrow{T}_{ij} \overleftrightarrow{T}_{jk} - \dots \right] \cdot \vec{E}}_{\text{induced moment}} \end{aligned} \quad (18)$$

The internal potential energy \mathcal{V} contains the individual potential energies of the lattice constituents, which includes Coulomb binding and London-van der Waals energies, is denoted by u_0 . The dipole-dipole interaction energy is separated out from the coulomb forces and denoted by u_{dip} . The induced contribution is u_{in} , and the internal energy due to field interaction with permanent dipoles is u_F [41]. Both u_{in} and u_F are strongly dependent on the external field, whereas u_{dip} indirectly depends on the external field due to internal fields from dipoles. Thus,

$$\begin{aligned} \mathcal{V} = & u_0 + u_{\text{dip}} + u_{\text{in}} + u_F \\ = & u_0 + \frac{1}{2} \vec{\mu} \cdot \overleftrightarrow{T} \cdot \vec{m}_0 + \frac{1}{2} \vec{E} \cdot \overleftrightarrow{A} \cdot \vec{E} - \vec{m}_0 \cdot \vec{E} \end{aligned} \quad (19)$$

where

$$\vec{m}_0 = [\overleftrightarrow{I} + \alpha \overleftrightarrow{T}]^{-1} \cdot \vec{\mu} = \overleftrightarrow{A} \cdot \overleftrightarrow{T} \cdot \vec{\mu} \quad (20)$$

$$u_{\text{dip}} + u_{\text{in}} = \frac{1}{2} \vec{\mu} \cdot \overleftrightarrow{T} \cdot \vec{m}_0 + \frac{1}{2} \vec{E} \cdot \overleftrightarrow{A} \cdot \vec{E} \quad (21)$$

In these equations \overleftrightarrow{T} and \vec{m} do not have subscripts, since we have combined all particles under a single variable to represent the 3 N dimensional system. The effective polarizability tensor, which includes intermolecular interactions, is defined as

$$\overleftrightarrow{A} = \alpha [\overleftrightarrow{I} + \alpha \overleftrightarrow{T}]^{-1} \quad (22)$$

We see that the electronic energy consists of field independent terms plus terms that depend on the electric field.

The total dipole moment is a sum of a permanent moment and an induced component. The total static dipole-moment density including permanent moments can be written as

$$\vec{p}' = \frac{1}{V} [\vec{p}_0 + \vec{A} \cdot \vec{E}] \quad (23)$$

and therefore the potential energy is

$$\mathcal{V} = - \frac{u_0 + u_{\text{dip}}}{V} = - \vec{p}' \cdot \vec{E} \quad (24)$$

3.2 THE HAMILTONIAN

We now use the results from the previous subsection to develop the Hamiltonian. Consider a polarizable material immersed in an external electric field. The field $\vec{E}(\vec{r}, t)$ is turned on at $t = 0$, interacts with dipoles, and thereby drives the relaxation process. If quadrupoles and higher multipoles were included then electric field gradients also would be present in the Hamiltonian. We assume that the wavelength of the field is much longer than the particle dimensions. In a finite time after field application, relaxation occurs in the material which modifies the field interacting with the molecules. Constitutive relations exist between net polarization and the applied field. In this classical analysis I limit the frequency to $f \ll kT/h2\pi$ (e.g. $f < 100$ GHz). The corresponding relaxation time is $\tau \gg h/kT$, or $\gtrsim 1$ ps. Using the expression for the kinetic energy density,

$$G/V = \sum_i \frac{\vec{\pi}_i \cdot \vec{\pi}_i}{2M_i} \delta(\vec{r} - \vec{r}_i) \quad (25)$$

the Hamiltonian, in volume V , which includes dipolar interaction (15), can be written as

$$\begin{aligned} \mathcal{H}(t) &= \int d^3r \{ \underbrace{\mathcal{U}(\vec{r}, t)}_{\text{lattice-energy}} - \underbrace{\vec{p}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t)}_{\text{dipolar-energy}} \} \\ &= \sum_i u_{0(i)}(\vec{r}_i) - \sum_{i \neq j} u_{\text{dip}(ij)}(\vec{r}_i - \vec{r}_j) \\ &\quad + \sum_{i=1}^N \sum_{j=1}^3 \frac{\pi_{ji}^2}{2M_i} - \sum_{i=1}^N q_i \vec{r}_i \cdot \vec{E}(\vec{r}_i, t) \end{aligned} \quad (26)$$

where Γ denotes phase-space variables. \mathcal{U} is the lattice part of the potential energy, excluding the electric field interaction with the dipole moment, and contains charge interactions, dipole-dipole interactions, van der Waals energy, and the kinetic energy of the lattice. The dipole-dipole interaction depends on the external electric field indirectly through the dipole moment. In classical mechanics the dynamical state is specified by the phase coordinates \vec{r}_i and momenta $\vec{\pi}_i$ for each degree of freedom at a particular time. \vec{p} given in (15) contains the effects of both the permanent and induced dipole moments.

3.3 POLARIZATION EVOLUTION EQUATION

The goal in this section is to derive evolution equations using a previously developed formalism [1] (see Section 7.3). Using expected values of the polarization and internal energy as constraints, a canonical-density function $\sigma(t)$ will be developed.

The local dipole-moment density $\vec{p}(\vec{r})$ and internal energy density $\mathcal{U}(\vec{r})$ do not explicitly depend on time, but it enters through the implicit dependence in $\vec{\pi}_i$ and \vec{r}_i . The time dependence is obtained when the expectation of these quantities is taken. The time evolution will be obtained from the Liouville equation. The constraints on the average polarization and internal energy density at time t are

$$\langle \vec{P}(\vec{r}, t) \rangle = \text{Tr}_r(\vec{p}(\vec{r}, \Gamma) \sigma(\Gamma, t)) \equiv \langle \vec{p} \rangle_t \quad (27)$$

$$U(\vec{r}, t) = \text{Tr}_r(\mathcal{U}(\vec{r}, \Gamma) \sigma(\Gamma, t)) \equiv \langle \mathcal{U} \rangle_t \quad (28)$$

The definition of the trace is

$$\text{Tr}_r(\cdot) \equiv \int (\cdot) \Pi_i d\vec{r}_i d\vec{\pi}_i \equiv \int (\cdot) d\Gamma \quad (29)$$

The trace Tr_r is defined in classical mechanics as integration over phase variables and quantum mechanically as a trace of the operators. The canonical density function, at a single instant in time, for dielectric response, can be constructed by maximizing the information entropy

$$S(t) = -kT_r(\sigma(t) \ln \sigma(t)) \quad (30)$$

subject to constraints (27) and (28) which yields [1]

$$\sigma(\Gamma, t) = \frac{\exp(-\int d^3r \{ \beta \mathcal{U}(\vec{r}, \Gamma) - \beta \vec{p}(\vec{r}, \Gamma) \cdot \vec{E}_P(\vec{r}, t) \})}{Z} \quad (31)$$

where

$$Z = \text{Tr}_r \left(\exp \left[- \int d^3r \{ \beta \mathcal{U}(\vec{r}, \Gamma) - \beta \vec{p}(\vec{r}, \Gamma) \cdot \vec{E}_P(\vec{r}, t) \} \right] \right) \quad (32)$$

and the Lagrangian multiplier β is expressed in terms of temperature $\beta(\vec{r}, t) = 1/kT(\vec{r}, t)$, k is Boltzmann's constant and $-\beta \vec{E}_P$ is another Lagrangian multiplier. The Lagrangian multipliers are thermodynamic conjugates of $U(\vec{r}, t)$ and $\vec{P}(\vec{r}, t)$ and are functions of \vec{r} and t . \vec{E}_P can be interpreted as an effective local field, in contrast to \vec{E} which is the external field (see Figure 2).

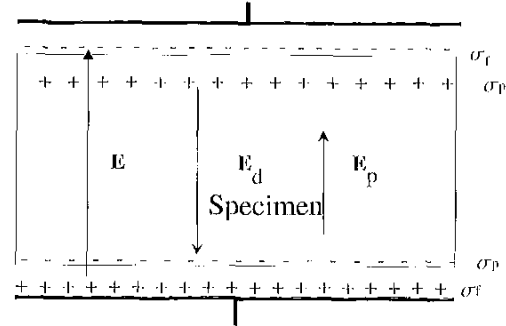


Figure 2. Electric fields in a capacitor that contains a polarizable material. The field without material is \vec{E} , the depolarizing field is \vec{E}_d , and local electric field is \vec{E}_p . The free and bound surface-charge densities are σ_f and σ_p .

The fields \vec{E} and \vec{E}_p in Figure 2 differ due to redistribution of charge in the presence of the applied field causing a depolarization field that tends to decrease the net electric field in the material.

The full statistical-density function ρ that satisfies Liouville's equation (Section 7.3, Equation (97)) can be expressed in terms of the canonical density function as given in Section 7.3 Equation (104) and repro-

duced here

$$\rho(\Gamma, t) = \sigma(\Gamma, t) - \int_0^t d\tau T(t, \tau) \mathcal{L}(\Gamma, \tau) \sigma(\Gamma, \tau) \quad (33)$$

where T is an evolution operator and \mathcal{L} is Liouville's operator (see Section 7.3 for a review of the projection-operator formalism). The explicit projection operator dependence has vanished in (33) since

$$\langle \dot{\vec{p}} \rangle \equiv T_r(i\mathcal{L}\vec{p}) = \dot{\vec{0}} = \langle \dot{\mathcal{U}} \rangle \quad (34)$$

as shown in Section 7.2 using the definition of the projection operator. The dot is defined in Section 7.3. The projection operator still influences T in spite of (34). The relation $\langle \dot{\vec{p}} \rangle = \dot{\vec{0}}$ would hold even if the quadrupole and higher-order moments were included in the definition of \vec{p} . The projection operator promotes convergence of the kernel at long times.

In magnetics a reversible term arises due to the noncommutivity of the spin components. Spin precession obeys a torque equation. No analogous dynamical evolution is followed in dielectric relaxation.

If we apply (106) and (95) from Section 7.3 we find

$$\frac{\partial \vec{P}(\vec{r}, t)}{\partial t} = \int d^3 r' \int_0^t T_r \left([\vec{p}(\vec{r}', t), G(\vec{r}, t)] T(\Gamma, t, \tau) \times \left[\vec{p}(\vec{r}', \tau), \sigma(\Gamma, \tau) \right] \right) \cdot \{ \vec{E}(\vec{r}', \tau) - \vec{E}_P(\vec{r}', \tau) \} d\tau \quad (35)$$

and the internal energy density evolution is given by

$$\frac{\partial U(\vec{r}, t)}{\partial t} = \vec{E}(\vec{r}, t) \cdot \frac{\partial \vec{P}(\vec{r}, t)}{\partial t} \quad (36)$$

Actual calculation using (35) and (36) is difficult. We will make simplifications in the next Sections. The memory kernel is defined as

$$\bar{K}_c = T_r \left([\vec{p}(\vec{r}, t), G(\vec{r}, t)] T(\Gamma, t, \tau) [\vec{p}(\vec{r}', \tau), \sigma(\Gamma, \tau)] \right) \quad (37)$$

Here, I have indicated the implicit time dependence in \vec{p} and G . I use the symbols $[\]$ for classical-mechanical Poisson brackets and I have used (34). Equations (35) and (36) are very general and are valid for non-equilibrium states. An interesting feature of (35) is that the time rate of change of the average polarization is proportional to the difference between the external and effective local fields. Equations (27), (28), (35), and (36) are to be solved together for \vec{P} , U , β , and $-\beta \vec{E}_P$. Equation (36) is an equation for conservation of energy.

We can also calculate the non-equilibrium entropy from (30)

$$S(t) = -k T_r (\sigma(t) \ln \sigma(t)) \\ = \int d^3 r \frac{1}{T} \left[U(\vec{r}, t) - \vec{P}(\vec{r}, t) \cdot \vec{E}_P(\vec{r}, t) \right] + k \ln Z \quad (38)$$

The entropy rate is

$$\frac{dS(t)}{dt} = -k T_r \left(\frac{d\sigma(t)}{dt} \ln \sigma(t) \right) \\ = \int d^3 r \frac{1}{T} \left[\frac{\partial \vec{P}(\vec{r}, t)}{\partial t} \cdot (\vec{E}(\vec{r}, t) - \vec{E}_P(\vec{r}, t)) \right] \quad (39)$$

Since $T dS/dt$ is the power absorbed by the media, the entropy production can be studied experimentally by (39) using (35) in the time or frequency domains.

The microscopic current density $\vec{J}(\vec{r})$, calculated in Section 7.1, is

$$\vec{J}(\vec{r}) = \sum_i^N \vec{J}_i = [\vec{p}(\vec{r}), G] \\ = \sum_{i=1}^N \left[\underbrace{\frac{\vec{\pi}_i}{M_i} q_i \delta(\vec{r}_i - \vec{r})}_{\text{charge current}} + \underbrace{\vec{r}_i \vec{\pi}_i \cdot \nabla \delta(\vec{r}_i - \vec{r})}_{\text{dipole current}} \right] \quad (40)$$

where M_i is mass, and the momentum of particle i is

$$\vec{\pi}_i = \sum_{j=1}^3 \pi_{ji} \vec{e}_j \quad (41)$$

where \vec{e}_j are unit vectors. This current density is due to the interaction of particle momenta with the polarization.

The Poisson brackets in (35) and (36) can be simplified

$$[\vec{p}(\vec{r}), \sigma] = \sum_i \beta(\vec{r}_i, t) \vec{J}_i(\vec{r}) \sigma \quad (42)$$

and

$$[\vec{p}(\vec{r}), \mathcal{U}] = [\vec{p}(\vec{r}), G] = \vec{J} \quad (43)$$

We can also express (35) in terms of reduced correlations using (40), (42), (43)

$$\frac{\partial \vec{P}(\vec{r}, t)}{\partial t} = \int_0^t \sum_j \left[\bar{f}_{1j}(\vec{r}, t, \tau) (\vec{E}(\vec{r}_j, \tau) - \vec{E}_P(\vec{r}_j, \tau)) \right. \\ \left. - \bar{f}_{2j}(\vec{r}, t, \tau) : (\nabla \vec{E}(\vec{r}_j, \tau) - \nabla \vec{E}_P(\vec{r}_j, \tau)) \right] d\tau \quad (44)$$

where the sum is over all particles, and the reduced correlation functions are

$$\bar{f}_{1j}(\vec{r}, t, \tau) = \frac{\beta(\vec{r}_j, \tau) q_j}{M_j} \times \\ \sum_{i=1}^N T_r \left(\vec{J}_i(\vec{r}_i, t) T(\Gamma, t, \tau) \vec{\pi}_j(\tau) \sigma(\Gamma, \tau) \right) \quad (45)$$

and

$$\bar{f}_{2j}(\vec{r}, t, \tau) = \frac{\beta(\vec{r}_j, \tau) q_j}{M_j} \times \\ \sum_{i=1}^N T_r \left(\vec{J}_i(\vec{r}_i, t) T(\Gamma, t, \tau) \vec{r}_j \vec{\pi}_j(\tau) \sigma(\Gamma, \tau) \right) \quad (46)$$

The $j = i$ term in (45) is interpreted as the single-particle or intra-cluster correlation and the $j \neq i$ terms correspond to the interparticle or intercluster correlations. The second term in (44) is the interaction with the gradient of the electric field.

3.4 LINEAR APPROXIMATION

In order to use (35) and (36) we need to obtain the Lagrangian multiplier for the effective local field $\vec{E}_P(\vec{r}, t)$. The goal of this section is to obtain an approximation for \vec{E}_P .

In a linear approximation to (27) we use a zero-order equilibrium canonical-density function

$$\sigma_0 = \frac{\exp(-\beta u_0)}{T_r(\exp(-\beta u_0))} \quad (47)$$

If we expand (27), assume u_{dip} and $\vec{p} \cdot \vec{E}_P$ are small relative to kT , and keep only terms linear in \vec{E}_P , we find

$$\begin{aligned} \vec{P}(\vec{r}, t) &\approx V \{ \beta \langle \vec{p} \vec{p} \rangle_0 - 2\beta^2 \langle \vec{p} \vec{p} u_{\text{dip}} \rangle_0 \} \cdot \\ \vec{E}_P(\vec{r}, t) &= \vec{\chi}_0 \cdot (\vec{I} + \vec{N}) \cdot \vec{E}_P(\vec{r}, t) \end{aligned} \quad (48)$$

where the zero-order static susceptibility is $\vec{\chi}_0 = \beta V \langle \vec{p} \vec{p} \rangle_0$.

I have assumed the material is nonpyroelectric, so there is no net polarization in the absence of a field and

$$\begin{aligned} \vec{N} &= 2\beta \{ \langle \vec{p} \vec{p} \rangle_0 \}^{-1} \langle \vec{p} \vec{p} u_{\text{dip}} \rangle_0 \\ &= 2V\beta^2 \vec{\chi}_0^{-1} \langle \vec{p} \vec{p} u_{\text{dip}} \rangle_0 \end{aligned} \quad (49)$$

Assuming \vec{N} is small, since $u_{\text{dip}}/kT \ll 1$, we may expand (48) to obtain the effective local field

$$\begin{aligned} \vec{E}_P(\vec{r}, t) &\approx (\vec{I} + \vec{N}) \vec{\chi}_0^{-1} \vec{P}(\vec{r}, t) \\ &= \vec{\chi}_0^{-1} \vec{P}(\vec{r}, t) - \vec{L} \cdot \vec{P}(\vec{r}, t) \end{aligned} \quad (50)$$

where the depolarization tensor is defined as

$$\vec{L} = -2V\beta^2 \vec{\chi}_0^{-1} \langle \vec{p} \vec{p} u_{\text{dip}} \rangle_0 \vec{\chi}_0^{-1} = -\vec{N} \vec{\chi}_0^{-1} \quad (51)$$

Equation (51) is an expression for the depolarization tensor in terms of the dipole-dipole interaction potential energy.

Depolarization has its origin in the potential field created by the polarized bound and free charge which creates an opposing electric field. The local field is a linear combination of the external field plus the negative gradient of the potential caused by the free and bound charge. We can see this using a derivation given by de Groot [5] for a general local field \vec{E}_L in terms of a polarization field \vec{P} , a potential due to polarized charge q_{pol} and an external electric field \vec{E}

$$\begin{aligned} \vec{E}_L &= \vec{E} + \underbrace{\nabla \cdot \frac{1}{4\pi\epsilon} \int_V \frac{\nabla' \cdot \vec{P}(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d\vec{r}'}_{-\phi_P} \\ &= \vec{E} + \underbrace{\int_V \nabla \nabla' \cdot \frac{1}{4\pi\epsilon |\vec{r} - \vec{r}'|} d\vec{r}' \cdot \vec{P}(\vec{r}', t)}_{-\vec{L}} \end{aligned} \quad (52)$$

Here we have identified the depolarization tensor \vec{L} which is the negative of the volume integral of the dipole-dipole interaction tensor between dipoles located at \vec{r}_i and \vec{r}_j .

4 RELAXATION

4.1 AN APPROXIMATION TO THE POLARIZATION EQUATION

The goal of this Section is to examine the evolution Equations (35) and (36) and to study the susceptibility using (35), (36), (50), (51), (42), and (43).

Suppressing spatial dependence, we have the generalized evolution equations

$$\begin{aligned} \frac{d\vec{P}(t)}{dt} &= V \int_0^t \{ \beta \vec{L}_r \cdot [\vec{J}(t) \mathcal{T}(t, \tau) \cdot \vec{J}(\tau) \sigma(\tau)] \times \\ &[(\vec{I} + \vec{L} \cdot \vec{\chi}_0) \vec{\chi}_0^{-1} \cdot (\vec{P}(\tau) - \vec{\chi}_0 (\vec{I} + \vec{L} \vec{\chi}_0)^{-1} \times \\ &\vec{E}(\tau))] d\tau = 0 \end{aligned} \quad (53)$$

and

$$\begin{aligned} \frac{dU(t)}{dt} &= V \int_0^t \{ \vec{E}(t) \cdot \beta \vec{L}_r \cdot (\vec{J}(t) \mathcal{T}(t, \tau) \cdot \vec{J}(\tau) \sigma(\tau)) \times \\ &[(\vec{I} + \vec{L} \cdot \vec{\chi}_0) \vec{\chi}_0^{-1} \cdot (\vec{P}(\tau) \\ &- \vec{\chi}_0 (\vec{I} + \vec{L} \cdot \vec{\chi}_0)^{-1} \cdot \vec{E}(\tau))] d\tau = 0 \end{aligned} \quad (54)$$

Due to the approximation on the local field, (53) and (54) are not exact, but the approximations made are not severe. Equation (53) has the form of a generalized Debye equation. The kernel K_c is a current-current correlation function. In a linear approximation the kernel in (53) depends only on $t - \tau$. It can be shown to be real and an even function of time [42, 43] (although in many phenomenological theories the correlation function is not even in time). Harp and Berne [43] and Bliot and Constant [19, 44] have studied memory functions in molecular-dynamical calculations in the forms of delta function, exponential, and Gaussian.

4.2 THE POLARIZATION CURRENT AND SUSCEPTIBILITY

4.2.1 SUSCEPTIBILITY

In this Section I study the kernel \vec{K}_c and look at special cases of relaxation behavior. The susceptibility $\vec{\chi}$ due to an external field $\vec{E}(\omega)$ is defined by

$$\mathcal{F}\{\vec{P}\}(\omega) = \vec{\chi}(\omega) \cdot \vec{E}(\omega) \quad (55)$$

The susceptibility of (53) is

$$\begin{aligned} \vec{\chi} &= [\vec{\chi}_0^{-1} + \mathcal{F}\{\vec{K}_c\}(\omega)]^{-1} \times \\ &\mathcal{F}\{\vec{K}_c\}(\omega) \vec{\chi}_0 \cdot (\vec{I} + \vec{L} \cdot \vec{\chi}_0)^{-1} \end{aligned} \quad (56)$$

The Fourier transformed memory function models the frequency dependence of relaxation in a material and is in some respects more fundamental than the susceptibility. The memory function has been studied previously using Zwanzig's projection operator formalism [45]. Materials with a single relaxation time are adequately described by the Debye model, which has a Fourier transform of the memory function that is frequency independent. More complex materials require a frequency-dependent relaxation time. In fact a single, constant relaxation time is not consistent with the required high-frequency behavior of dielectrics since the imaginary part of the susceptibility must decrease faster than $1/\omega^2$. This behavior can be obtained if the relaxation time is frequency dependent.

Assuming a scalar kernel which is a function only of $t - \tau$, neglecting spatial dependence and depolarization in (53), we obtain

$$\begin{aligned}\chi(\omega) &= \chi_0 \frac{\mathcal{F}\{K_e\}(\omega)}{i\omega + \mathcal{F}\{K_e\}(\omega)} \\ &= \chi_0 \frac{h^2(\omega) + r^2(\omega) - \omega r(\omega)}{h^2(\omega) + [\omega - r(\omega)]^2} \\ &\quad - i\chi_0 \frac{\omega h(\omega)}{h^2(\omega) + [\omega - r(\omega)]^2}\end{aligned}\quad (57)$$

I have defined $\mathcal{F}\{K_e\}(\omega) =: h(\omega) + ir(\omega)$. Assuming the susceptibility is analytic in the frequency region of interest, causality requires the poles of χ to reside in the upper half plane. The susceptibility, subject to the approximation (50), must be of this form in (57) [46].

If we define a memory response function $dK(t)/dt = K_e(t)$,

$$\mathcal{F}\{K\}(\omega) = \frac{\mathcal{F}\{K_e\}(\omega)}{i\omega} \quad (58)$$

we see that

$$\chi(\omega) = \chi_0 \frac{\mathcal{F}\{K\}(\omega)}{1 + \mathcal{F}\{K\}(\omega)} \quad (59)$$

Equivalently, the Fourier transform of the memory response function can be written in terms of the susceptibility,

$$\mathcal{F}\{K\}(\omega) = \frac{\chi(\omega)/\chi_0}{1 + \chi(\omega)/\chi_0} \quad (60)$$

Assuming the susceptibility satisfies (59), taking the inverse Laplace transform we obtain

$$K(t) = \frac{1}{\chi_0} I(t) + \frac{1}{\chi_0} \int_0^t K(t - \tau) I(\tau) d\tau \quad (61)$$

By iteration of (61) we have

$$K(t) = \frac{1}{\chi_0} \left[I(t) + \frac{1}{\chi_0} \int_0^t I(t - \tau) I(\tau) d\tau + \dots \right] \quad (62)$$

Also the susceptibility satisfies (57) and taking the inverse Laplace transform we obtain

$$\frac{dI}{dt} = - \int_0^t K_e(t - \tau) I(\tau) d\tau + \chi_0 K_e(t) \quad (63)$$

where I is the inverse transform of the susceptibility. By iteration

$$K_e(t) = \chi_0 \left[\frac{dI}{dt} + \frac{1}{\chi_0} \frac{d}{dt} \int_0^t I(t - \tau) I(\tau) d\tau + \dots \right] \quad (64)$$

This equation can be used to obtain the response function in terms of the memory function K_e [45]. When $\chi_0 d\Phi(t)/dt = I(t)$ and $\Phi(0) = 1$

$$\frac{d\Phi}{dt} = - \int_0^t K_e(t - \tau) \Phi(\tau) d\tau \quad (65)$$

In Sections 4.2.2 to 4.2.5 we will discuss special cases of relaxation.

4.2.2 DEBYE RELAXATION

The relaxation kernel can be approximated in a number of ways. In the simplest case of a Markov process with a single relaxation time τ_e , the kernel is a delta function at $t = 0$, $K_e(t) = \delta(t) \bar{I}/\tau_e$. Using a simplistic approximation for the Lagrangian multiplier $\bar{I}_D = \bar{P}/\chi_0$ and neglecting depolarization, we obtain Debye's equation for the delta function response equation

$$\frac{d\bar{P}}{dt} + \frac{\{\bar{P} - \chi_0 \bar{I}\}}{\tau_e} = 0 \quad (66)$$

The response function in this case can be calculated from (63) to be

$$I(t) = \frac{\chi_0 \Theta(t) \exp(-t/\tau_e)}{\tau_e} \quad (67)$$

The memory function in this case can be derived exactly using the first two terms from (64), using (67), where $\Theta(t)$ is the unit step function. The Fourier transform of (66) yields

$$\chi(\omega) = \frac{\chi_0}{1 + i\omega\tau_e} \quad (68)$$

In this approximation the Fourier transformed memory function is

$$\mathcal{F}\{K_e\}(\omega) = \frac{1}{\tau_e} \quad (69)$$

We also note by analogy to (66) that the RHS of (35) relates to damping. We see that an extremely simple memory function leads to Debye relaxation which has constant memory.

4.2.3 EXPONENTIAL MEMORY FUNCTION

In this case

$$K_e = A\Theta(t) \frac{\exp(-|t|/\tau_e)}{\tau_e^2} \quad (70)$$

The Fourier transform yields

$$\mathcal{F}\{K_e\} = \frac{A}{\tau_e(1 + i\omega\tau_e)} \quad (71)$$

The response function can be calculated for this case to be a damped sinusoid

$$I(t) = A\Theta(t) \frac{\exp[-\frac{t}{2\tau_e}] \sin(\frac{\sqrt{3}t}{2\tau_e})}{\sqrt{3}\tau_e} \quad (72)$$

The susceptibility with $A = 1$ is

$$\chi(\omega) = \frac{\chi_0}{1 + i\omega\tau_e(1 + i\omega\tau_e)} \quad (73)$$

Note that this exponential memory function yields combined inertial and Debye relaxation. In this case the memory decreases as frequency increases.

4.2.4 GAUSSIAN MEMORY FUNCTION

In this case

$$K_e(t) = \frac{A}{\tau_e^2} \Theta(t) \exp(-\frac{t^2}{\tau_e^2}) \quad (74)$$

The Fourier transform is

$$\mathcal{F}\{K_e\}(\omega) = \frac{A\sqrt{\pi}}{2\tau_e} \exp\left(-\frac{\tau_e^2\omega^2}{4}\right) \left[1 + i \operatorname{erf}\left(\frac{\tau_e\omega}{2}\right)\right] \quad (75)$$

The susceptibility is

$$\chi(\omega) = \frac{\chi_0}{1 + i\omega/(\frac{A\sqrt{\pi}}{2\tau_e} \exp(-\frac{\tau_e^2\omega^2}{4}) [1 + i \operatorname{erf}(\frac{\tau_e\omega}{2})])} \quad (76)$$

where erf is the error function of imaginary argument.

4.2.5 POWER-LAW RELAXATION AND MEMORY FUNCTION

In the previous special cases the memory function was a simple function. In order to model dielectric data over large frequency bands, when there are a number of relaxation mechanisms involved, more comprehensive models are needed. As a last application we consider a dielectric represented by a lumped-circuit model and show how it reduces to the Dissado-Hill model. Using the Dissado-Hill approximation for the correlation function, we will develop an expression for the memory function. In this case, the expression for the Fourier transform of the memory function is not simple.

RC circuits have been used extensively to model dielectric response [26, 38, 47, 48]. The susceptibility in (57) takes the form of a generalized RC transfer function for a transmission line. In a simple lumped-circuit model the system function can be identified as

$$S = \frac{1}{1 + \frac{(C_L + i\omega C_L)(R + i\omega L)}{(C_L + i\omega C_L)(R + i\omega L)}} \quad (77)$$

where C_L , G_L , L , and R are lumped-circuit parameters.

This model is an overly simplistic representation of most dielectrics. The model can be generalized by assuming a fractal-like power-law dependence of the lumped-circuit elements.

First we note that the time-averaged inverse Fourier transform of the power-law generalization of the transfer term in (77) yields an expression for the time-response function in the same form as given in Dissado and Hill [49]

$$I(t) = \frac{A}{2\pi t} \Theta(t) \int_{-\infty}^{\infty} \frac{\exp(i\omega t) d\omega}{(G_L + i\omega C_L)^{1+m-n} (R + i\omega L)^{1-m}} \quad (78)$$

$$= \frac{A}{\Gamma_f(2-n) C_L^{1+m-n} L^{1-m}} \Theta(t) \exp(-t/\tau_1) t^{-n} \times$$

$$M[1-m, 2-n; \omega_p t]$$

where $\tau_1 = C_L/G_L$, $\tau_2 = L/R$, $\omega_p = 1/\tau_1 + 1/\tau_2$, M is the confluent hypergeometric function, and A is a constant. In the Dissado-Hill theory, $1/\tau_2 = R/L \rightarrow 0$. If R and L are included then the model is a generalization of the Dissado-Hill approach and can include magnetic effects. We also have when $L/R \rightarrow 0$ the response autocorrelation function

$$\Phi(t) = 1 + \frac{A\Gamma_f(1-n)}{C_L^{1+m-n} L^{1-m}} \Theta(t) t^{1-n} \times$$

$${}_2F_2[(1+m-n, 1-n), (2-n, 2-n), -\omega_p t] \quad (79)$$

At small times (78) has a limiting form of t^{-n} where $0 < n < 1$. At longer times, the limiting form is t^{-m-n-1} where $0 < m < 1$. I will now comment on the relationship between (78) and the Dissado-Hill result.

If we multiply both sides of (78) by t and take the Fourier transform of $tI(t)$ we have

$$\frac{1}{i} \frac{d\chi(\omega)}{d\omega} = \frac{A}{C_L^{1+m-n} L^{1-m}} \times$$

$$\frac{1}{(\frac{G_L}{C_L} + i\omega)^{1+m-n} (\frac{R}{L} + i\omega)^{1-m}} \quad (80)$$

and therefore by integration we obtain the susceptibility

$$\chi(\omega) = \chi_0 + iA^{1-m-n} L^{m-1} \times$$

$$\int_0^{\omega} \frac{1}{(\frac{G_L}{C_L} + ix)^{1+m-n} (\frac{R}{L} + ix)^{1-m}} dx \quad (81)$$

It is interesting to note that in this case the susceptibility at ω depends on the integral over ω of the fractional-power circuit function. Once the integral in (81) is evaluated, we see this equation is equivalent to the frequency-domain function given by Dissado and Hill [49] as $R/L \rightarrow 0$:

$$\chi(\omega) = \chi_0 [1 + i\frac{\omega}{\omega_p}]^{n-1} \times$$

$$\frac{{}_2F_1(1-n, 1-m, 2-n, [1 + i(\omega/\omega_p)]^{-1})}{{}_2F_1(1-n, 1-m, 2-n, 1)} \quad (82)$$

At low frequencies $\chi(\omega)$ in (82) behaves as ω^n , and at high frequencies, as ω^{n-1} .

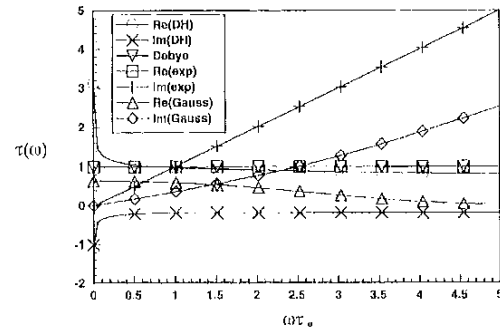


Figure 3. $\tau(\omega)$ for Debye relaxation, Dissado-Hill theory with $m = 0.8$, $n = 0.2$, exponential (exp), and Gaussian (Gauss).

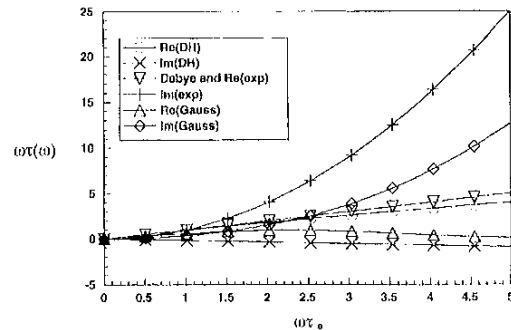


Figure 4. The nondimensional variable $\omega\tau(\omega)$ for Debye relaxation, Dissado-Hill theory with $m = 0.8$, $n = 0.2$, exponential (exp), and Gaussian (Gauss).

5 THE MEMORY FUNCTION AND FREQUENCY DEPENDENCE OF RELAXATION TIMES

We now study the Fourier transform of the memory function for the various cases. The relationship of $\mathcal{F}\{K_e\}(\omega)$ to χ can be evaluated from (57),

$$\mathcal{F}\{K_e\}(\omega) = i\omega \frac{\chi(\omega)}{\chi_0 - \chi(\omega)} \quad (83)$$

For the Dissado-Hill function the Fourier transform of the memory function is

$$\mathcal{F}\{K_c\}(\omega) = i\omega \times \frac{{}_2F_1(1-n, 1-m, 2-n, [1+i(\omega/\omega_p)]^{-1})}{{}_2F_1(1-n, 1-m, 2-n, 1)} \frac{1}{[1+i\omega/\omega_p]^{1-n} \dots \frac{{}_2F_1(1-n, 1-m, 2-n, [1+i(\omega/\omega_p)]^{-1})}{{}_2F_1(1-n, 1-m, 2-n, 1)}}} \quad (84)$$

We can obtain additional insight into the behavior of the memory function if we define the complex relaxation time $\tau(\omega)$ as

$$\frac{1}{\mathcal{F}\{K_c\}} \equiv \tau_r(\omega) + i\tau_i(\omega) \equiv \tau(\omega) \quad (85)$$

The susceptibility in this case is

$$\chi(\omega) = \chi_0 \frac{1 - \omega\tau_i(\omega)}{\omega^2\tau_r^2(\omega) + (1 - \omega\tau_i(\omega))^2} - i\chi_0 \frac{\omega\tau_r(\omega)}{\omega^2\tau_r^2(\omega) + (1 - \omega\tau_i(\omega))^2} \quad (86)$$

In a Debye relaxation, the relaxation time is τ_c which is independent of frequency, as indicated in (69) and is shown in Figures (3) and (4); we also plot the relaxation times for exponential, Gaussian, and Dissado-Hill functions. Note that the Dissado-Hill function has both real and imaginary parts and has unique and significant frequency dependence. This is due to limiting behaviors of the correlation function in (1) and (2).

6 CONCLUSIONS

IN this paper a statistical-mechanical theory for polarization evolution for a system of particles was derived using a projection-operator approach. New generalized equations of motion, nonlocal in space and time, have been derived for the polarization and internal energy, which includes effects of memory and non-equilibrium.

The internal energy was studied and decomposed into lattice potential energy, kinetic energy, and energy due to permanent and induced dipole moments. The main difficulty with the present approach is the estimation of the memory function.

A linear approximation to the polarization was developed which involves the depolarization tensor. The resulting equation of motion in a linear approximation was time-invariant and causal. The effective local field was developed in terms of the relaxation kernel. The linear-response function was related to the kernel and then the Fourier transform of the kernel was related to the Fourier transformed memory function. It was shown that the susceptibility must be a specific function of the Fourier transform of the memory function. The Fourier transformed memory function and frequency-dependent relaxation time were developed for special cases and related to the susceptibility.

When studying physical mechanisms of relaxation, in many respects, the Fourier transform of the memory function appears to be more fundamental than the susceptibility. Very simple forms of the memory function yield classical dielectric behavior. We found that when the memory kernel can be written in terms of a delta function in time, we recover the Debye equation. In the case of an exponential memory function we obtain a Debye-like susceptibility that incorporates inertial effects. In another application, where we have a power-law circuit transfer function, we obtain the same susceptibility as Dissado and Hill

[49] and develop an equation for the Fourier transform of the memory function. It was found that for the Dissado-Hill model the susceptibility is given by an integral over frequency of the transfer function. The memory function in this case is much more complicated as a result of this model incorporating a number of relaxation mechanisms.

ACKNOWLEDGMENT

I would like to thank Dr. Baldwin Robertson for interactions with the various aspects of his projection-operator theory and Bill Riddle for graphical support and Dr. Lorant Muth for comments.

7 APPENDIX

7.1 KINETIC ENERGY OF THE LATTICE

The Poisson brackets for position and momentum satisfy

$$[r_i, r_j] = [\pi_i, \pi_j] = 0 \quad (87)$$

$$[\pi_j, r_j] = \delta_{ij} = -[r_i, \pi_j] \quad (88)$$

The kinetic energy is

$$G = \sum_{i=1}^N \sum_{j=1}^3 \frac{\pi_{ji}^2}{2M_i} \quad (89)$$

If we use (15) for the dipole-moment density

$$\vec{p}(\vec{r}) = \sum_i \vec{r}_i q_i \delta(\vec{r}_i - \vec{r}) \quad (90)$$

Using Poisson brackets

$$[r_{kl}, \pi_{ji}^2] = -2\pi_{ji}\delta_{jk}\delta_{li} \quad (91)$$

Therefore the current density is

$$\vec{J}(\vec{r}) = [\vec{p}(\vec{r}), G] = \sum_{i=1}^N \underbrace{\left[\frac{\vec{\pi}_i}{M_i} q_i \delta(\vec{r}_i - \vec{r}) \right]}_{\text{charge current}} \cdot \underbrace{\left[\frac{q_i}{M_i} \vec{r}_i \vec{\pi}_i \cdot \nabla \delta(\vec{r}_i - \vec{r}) \right]}_{\text{dipole current}} \quad (92)$$

Also, since the potential energy of the lattice is a function only of r_i

$$[\vec{p}, V] = 0 \quad (93)$$

7.2 REVERSIBLE TERM

Since

$$[\mathcal{U} \cdot \vec{p} \cdot \vec{E}_D, \sigma] = 0 \quad (94)$$

therefore

$$[\mathcal{U}, \sigma] = [\vec{p} \cdot \vec{E}_D, \sigma] \quad (95)$$

and

$$\begin{aligned} \langle \vec{p} \rangle &= T_r(\vec{p}[\mathcal{H}, \sigma]) = T_r(\vec{p}[\mathcal{U}, \sigma]) \\ &= [\vec{p} \cdot \vec{E}_D, \sigma] = T_r(\sigma[\vec{p}, \vec{p} \cdot (\vec{E}_D + \vec{E})]) = 0 \end{aligned} \quad (96)$$

Similarly, we can show that $\langle \mathcal{U} \rangle = 0$.

7.3 NON-EQUILIBRIUM PROBABILITY-DENSITY FUNCTION

In this section the projection-operator tools needed for studying relaxation processes treated in this paper are overviewed (see Robertson [50]). We suppress any spatial dependence and use a classical analysis.

The evolution of the statistical density function produced by the dynamics is given both classically and quantum mechanically by

$$\frac{\partial \rho(t)}{\partial t} = i[\mathcal{H}(t), \rho] = i\mathcal{L}(t)\rho(t) \quad (97)$$

Here \mathcal{L} is either the classical or quantum-mechanical Liouville operator.

We assume the set $\{P_j(\vec{r})\}$ of classical functions in phase space have expectations that are observable. The expectations are defined by $\langle P \rangle_t = T_r(P\rho(t))$. We define a generalized canonical density $\sigma(t)$ that describes the non-equilibrium thermodynamic variables of the system. Following [1, 50], the generalized canonical probability density function $\sigma(t)$ at time t satisfies

$$T_r(P_j(1')\sigma(t)) = \langle P_j(1') \rangle_t \quad (98)$$

In this approach $\sigma(t)$ is that part of the non-equilibrium statistical density $\rho(t)$ which is obtained from information at a single instant of time.

The canonical-density function is developed by use of constraint conditions (98) and by maximizing the information entropy to obtain

$$\sigma(t) = \exp(-\lambda * P') \quad (99)$$

The $*$ operator is defined as

$$\lambda * P' = \sum_{n=1}^N \lambda_n(t) P'_n \quad (100)$$

The Lagrangian multipliers $\lambda_j(t)$ are found by substitution of the calculated expectation values into the constraint conditions (98). Normalization is obtained by setting $P'_0 = 1$.

It is necessary to introduce a projection-like operator $P(t)$ that satisfies $P^2 = P$ [42]. The operator P is linear, non-Hermitian, and is used for separating relevant or observable details from irrelevant details. It satisfies both

$$\frac{\partial \sigma}{\partial t} = P(t) \frac{\partial \rho}{\partial t} \quad (101)$$

and

$$\sigma(t) = P(t)\rho(t) \quad (102)$$

and it is defined for operations on a function A by

$$P(t)A = \frac{\delta \sigma(t)}{\delta \langle P' \rangle_t} * T_r(P'A) \quad (103)$$

$$= P'\sigma * \langle P'P' \rangle_t^{-1} * \langle P'A \rangle_t$$

where δ denotes functional differentiation. The subscript t indicates that the expectation uses $\sigma(t)$. The operator P , a generalization of Zwanzig's time independent projection operator [42], separates out the relevant from the irrelevant part. The time correlation functions of the commonly used Kirkwood, Green, and Kubo expression for transport coefficients do not contain the projection operator and therefore do not have the correct behavior at long times. The projection operator also

contributes to the time dependence of $T(t, \tau)$. $P(t)$ may be expected to correct for the divergence of transport coefficients.

It is possible to show that with the condition, $\rho(0) = \sigma(0)$ [51]

$$\rho(t) = \sigma(t) - \int_0^t d\tau \mathcal{T}(t, \tau) \{1 - P(\tau)\} i\mathcal{L}(\tau) \sigma(\tau) \quad (104)$$

The integrating factor $\mathcal{T}(t, \tau)$ satisfies the initial value problem

$$\frac{\partial \mathcal{T}(t, \tau)}{\partial \tau} = \mathcal{T}(t, \tau) \{1 - P(\tau)\} i\mathcal{L} \quad (105)$$

with initial condition $\mathcal{T}(t, t) = 1$. All of the operators \mathcal{T} , P , and \mathcal{L} are linear.

Using this formalism an equation of motion can be written

$$\begin{aligned} \frac{\partial \langle P'_m \rangle_t}{\partial t} &= \langle \dot{P}'_m \rangle_t \\ &- \int_0^t T_r([\mathcal{H}, P'_m] \mathcal{T}(1 - P) [\mathcal{H}, \sigma(\tau)]) d\tau \end{aligned} \quad (106)$$

Here the dot is defined by $\dot{P}' = i\mathcal{L}P'$. The first term on the right side of (106) is the reversible or convection term; the second is the relaxation term. Equation (106) is exact. This technique has been used for other applications [52].

REFERENCES

- [1] B. Robertson, "Equations of motion in nonequilibrium statistical mechanics", *Phys. Rev.*, Vol. 144, pp. 151-161, April 1966.
- [2] R. A. Piccirelli, "Theory of the dynamics of simple fluids for large spatial gradients and long memory", *Physical Review*, Vol. 175, pp. 77-98, November 1968.
- [3] P. Mazur and B. R. A. Nijboer, "On the statistical mechanics of matter in an electromagnetic field: I", *Physica*, Vol. 14, pp. 971-986, 1953.
- [4] L. Rosenfeld, *Theory of Electrons*. Amsterdam: North-Holland Publ. Co., 1951.
- [5] S. R. de Groot and L. G. Suttorp, *Foundations of Electrodynamics*. New York: American Elsevier, 1972.
- [6] E. N. H. Robinson, *Macroscopic Electromagnetism*. Oxford: Pergamon Press, 1973.
- [7] J. D. Jackson, *Classical Electrodynamics*. New York: John Wiley and Sons, 1974.
- [8] R. H. Cole, "Correlation function theory of dielectric relaxation", *J. Chem. Phys.*, Vol. 42, pp. 637-643, 1964.
- [9] R. H. Cole, "Molecular correlation function approaches to dielectric relaxation", in *Physics of Dielectric Solids*, (Cambridge, MA), pp. 1-21, Institute of Physics, 1980.
- [10] R. Kubo, "Statistical-mechanical theory of irreversible processes: I", *J. Phys. Soc.*, Vol. 6, pp. 570-586, 1957.
- [11] R. Kubo, *Statistical Mechanics of Equilibrium and Nonequilibrium*. Amsterdam: North-Holland, 1965.
- [12] A. K. Jonscher, "The universal dielectric response and its physical significance", *IEEE Trans. Elec. Insul.*, Vol. 27, pp. 407-423, 1992.
- [13] L. A. Dissado and R. M. Hill, "Anomalous low frequency dispersion", *Chem. Soc. Faraday Trans. 2*, Vol. 80, pp. 291-318, 1984.
- [14] V. L. Gurevich and A. K. Tagantsev, "Intrinsic dielectric loss in crystals", *Advances in Physics*, Vol. 40, no. 6, pp. 719-767, 1991.
- [15] V. L. Gurevich, "Dielectric loss in crystals", *Sov. Phys. Solid State*, Vol. 21, no. 11, p. 1993-1998, 1979.
- [16] H. Scher and E. Montroll, "Anomalous transient-time dispersion in amorphous solids", *Phys. Rev.*, Vol. B12, pp. 2455-2465, 1975.
- [17] A. Hunt, "Comment on 'a probabilistic mechanism hidden behind the universal power law for dielectric relaxation: general relaxation equation'", *J. Phys. Condens. Matter*, Vol. 4, pp. 10503-10512, 1992.
- [18] A. Hunt, "One dimensional hopping conductivity calculations", *Philosophical Magazine B*, Vol. 64, pp. 327-334, 1991.

- [19] C. J. F. Bottcher and P. Bordewijk, *Theory of Electric Polarization: Volume 2*, Vol. I and II. New York: Elsevier, 1978.
- [20] G. F. Ferreira and B. Gross, "Comments on the dielectric theory: Non-Debye models and the superposition principle", *J. Appl. Phys.*, Vol. 68, pp. 2526-2528, 1990.
- [21] H. Kliem, "A comment on dielectric theory: Differential equations and permittivity", *J. Appl. Phys.*, Vol. 70, pp. 1861-1862, 1991.
- [22] L. A. Dissado, R. R. Nigmatullin, and R. M. Hill, *Dynamical Processes in Condensed Matter*, Chap. 3. New York: John Wiley and Sons, 1985.
- [23] J. van Turnhout, "Notes on distribution function", unpublished, 1980. Communication with Robert Hill.
- [24] G. Roussey, E. Spaak, and J.-M. Thiebaut, "Universal equation for the effective complex permittivity of mixtures valid for dielectric-dielectric and dielectric-conductor mixtures", *Phys. Rev B*, Vol. 46, pp. 452-455, November 1992.
- [25] G. Roussey, E. Spaak, and J.-M. Thiebaut, "Expression of the distribution function of relaxation times associated with the universal dielectric response", *J. Mole. Liq.*, Vol. 59, pp. 27-35, 1994.
- [26] L. A. Dissado and R. M. Hill, "The fractal nature of the cluster model dielectric response functions", *J. Appl. Phys.*, Vol. 66, pp. 2511-2524, 1989.
- [27] A. K. Jonscher, "A many-body model of dielectric polarization in solids", *Phys. Stat. Sol. (b)*, Vol. 83, pp. 585-597, 1977.
- [28] J. E. Anderson, "Model calculations of cooperative motions in chain molecules", *J. Chem. Phys.*, Vol. 52, pp. 2821-2830, 1970.
- [29] J. E. Shore and R. Zwanig, "Dielectric relaxation and dynamic susceptibility of one-dimensional modes for perpendicular-dipole polymers", *J. Chem. Phys.*, Vol. 63, pp. 5445-5458, 1975.
- [30] S. H. Glarum, "Dielectric relaxation in polar liquids", *J. Chem. Phys.*, Vol. 33, pp. 1371-1375, 1960.
- [31] J. L. Skinner, "Solitons, defect diffusion, and dielectric relaxation of polymers", *J. Chem. Phys.*, Vol. 73, pp. 4022-4026, 1980.
- [32] K. Weron and A. Jurelewicz, "Two forms of self-similarity as a fundamental feature of the power-law dielectric response", *J. Phys. A*, Vol. 26, pp. 395-410, 1993.
- [33] M. O. Vlad, R. Metzler, T. F. Nonnenmacher, and M. C. Mackey, "Universality classes for asymptotic behavior of relaxation processes in systems with dynamical order: Dynamical generalizations of stretched exponential", *J. Math. Phys.*, Vol. 37, pp. 2279-2305, May 1996.
- [34] K. Weron, "A probabilistic mechanism behind the universal power-law for dielectric relaxation for dielectric response: general relaxation equation", *J. Phys. Condens. Matter*, Vol. 3, pp. 9151-9162, 1991.
- [35] V. Halpern, "Dielectric relaxation, the superposition principle, and age-dependent transition rates", *J. Phys. D: Appl. Phys.*, Vol. 25, pp. 1533-1537, 1992.
- [36] J. H. V. Vleck, *The Theory of Electric and Magnetic Susceptibilities*. London: Oxford Press, 1932.
- [37] P. A. M. Steeman, "A numerical Kramers-Kronig transform for the calculation of dielectric relaxation losses free from Ohmic conduction losses", *Colloid. Polym. Sci.*, Vol. 275, pp. 106-115, 1997.
- [38] A. K. Jonscher, *Dielectric Relaxation in Solids*. London: Chelsea Dielectrics Press, 1983.
- [39] L. Fonda, G. C. Ghirardi, and A. Rimini, "Decay theory of unstable systems", *Rep. Prog. Phys.*, Vol. 41, pp. 587-631, 1978.
- [40] E. B. Graham, J. Pierrus, and R. E. Raab, "Multipole moments and Maxwell's equations", *J. Phys. B: At. Opt. Phys.*, Vol. 25, pp. 4673-4684, 1992.
- [41] M. Mandel and P. Mazur, "On the molecular theory of dielectric relaxation", *Physica*, Vol. 24, pp. 116-128, 1958.
- [42] R. Zwanig, "Ensemble method in the theory of irreversibility", *J. Chem. Phys.*, Vol. 33, no. 5, pp. 1338-1341, 1960.
- [43] G. D. Harp and B. J. Berne, "Time-correlation functions and molecular dynamics", *Phys. Rev A*, Vol. 2, pp. 975-996, 1970.
- [44] F. Bliot and E. Constant, "Memory functions and rotational diffusion models for symmetric top molecules", *Chemical Physics Letters*, Vol. 18, pp. 253-257, 1973.
- [45] L. A. Dissado, R. R. Nigmatullin, and R. M. Hill, *Lectures in Theoretical Physics*, Vol. III. New York: John Wiley and Sons, 1961.
- [46] J. P. Boon, *Molecular Hydrodynamics*. New York: McGraw-Hill, 1980.
- [47] R. M. Hill, L. A. Dissado, and R. R. Nigmatullin, "Invariant behavior classes for the response of simple fractal circuits", *J. Phys. Condens. Matter*, Vol. 3, pp. 9773-9790, 1991.
- [48] B. H. Bodakian and R. M. Hill, "Imperfections in fractally scaled transmission lines", *J. Phys. D*, Vol. 30, pp. 1820-1826, June 1997.
- [49] L. A. Dissado and R. M. Hill, "The structure of imperfect materials and relaxation spectroscopy", *Proc. R. Soc. Lond.*, Vol. A390, pp. 131-180, 1983.
- [50] B. Robertson, "Nonequilibrium statistical mechanics", in *Physics and Probability: Essays in Honor of Edwin T. Jaynes* (W. T. Grandy and P. W. Milonni, eds.), p. 251, Cambridge University Press, 1992.
- [51] B. Robertson and W. C. Mitchell, "Equations of motion in nonequilibrium statistical mechanics. iii: Open systems", *J. Math. Phys.*, Vol. 12, pp. 563-568, March 1971.
- [52] B. Robertson, "Equations of motion of nuclear magnetism", *Phys. Rev.*, Vol. 153, pp. 391-403, January 1967.

Manuscript was received on 22 October 1999, in revised form 31 March 2000.